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14. ABSTRACT We have used a high-temperature flowing-afterglow Langmuir-probe apparatus to measure rate constants for electron attachment to halomethanes which attach electrons very inefficiently at room temperature, yielding Cl ⁻ ion product. We studied CH ₂ Cl ₂ (495–973 K), CF ₂ Cl ₂ (291–1105 K), and CF ₃ Cl (524–1004 K) and include our recent measurement for CH ₃ Cl (700–1100 K) in the discussion of the electron attachment results. The measured attachment rate constants show Arrhenius behavior in the temperature ranges examined, from which estimates of rate constants at 300 K may be made: CH ₂ Cl ₂ (1.8 × 10 ⁻¹³ cm ³ s ⁻¹), CH ₃ Cl (1.1 × 10 ⁻¹⁷ cm ³ s ⁻¹), and CF ₃ Cl (4.2 × 10 ⁻¹⁴ cm ³ s ⁻¹), all of which are difficult to measure directly. In the case of CF ₂ Cl ₂ , the room temperature rate constant was sufficiently large to be measured (1.6 × 10 ⁻⁹ cm ³ s ⁻¹). The Arrhenius plots yield activation energies for the attachment reactions: 390 ± 50 meV (CH ₂ Cl ₂), 124 ± 20 meV (CF ₂ Cl ₂), 670 ± 70 meV (CH ₃ Cl), and 406 ± 50 meV (CF ₃ Cl). Comparisons are made with existing data where available. G3 calculations were carried out to obtain reaction energetics. They show that the parent anions of CH ₂ Cl ₂ , CF ₂ Cl ₂ , CH ₃ Cl, and CF ₃ Cl are stable, though CH ₃ Cl ⁻ exists only as an electrostatically bound complex. © 2009 American Institute of Physics. [DOI: 10.1063/1.3212598]
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Electron attachment to halomethanes at high temperature: CH_2Cl_2 , CF_2Cl_2 , CH_3Cl , and CF_3Cl attachment rate constants up to 1100 K

Thomas M. Miller,^{a)} Jeffrey F. Friedman,^{b)} Linda C. Schaffer, and A. A. Viggiano
*Space Vehicles Directorate, Air Force Research Laboratory, 29 Randolph Road, Hanscom Air Force Base,
 Massachusetts 01731-3010, USA*

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We have used a high-temperature flowing-afterglow Langmuir-probe apparatus to measure rate constants for electron attachment to halomethanes which attach electrons very inefficiently at room temperature, yielding Cl^- ion product. We studied CH_2Cl_2 (495–973 K), CF_2Cl_2 (291–1105 K), and CF_3Cl (524–1004 K) and include our recent measurement for CH_3Cl (700–1100 K) in the discussion of the electron attachment results. The measured attachment rate constants show Arrhenius behavior in the temperature ranges examined, from which estimates of rate constants at 300 K may be made: CH_2Cl_2 ($1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), CH_3Cl ($1.1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$), and CF_3Cl ($4.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$), all of which are difficult to measure directly. In the case of CF_2Cl_2 , the room temperature rate constant was sufficiently large to be measured ($1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). The Arrhenius plots yield activation energies for the attachment reactions: $390 \pm 50 \text{ meV}$ (CH_2Cl_2), $124 \pm 20 \text{ meV}$ (CF_2Cl_2), $670 \pm 70 \text{ meV}$ (CH_3Cl), and $406 \pm 50 \text{ meV}$ (CF_3Cl). Comparisons are made with existing data where available. G3 calculations were carried out to obtain reaction energetics. They show that the parent anions of CH_2Cl_2 , CF_2Cl_2 , CH_3Cl , and CF_3Cl are stable, though CH_3Cl^- exists only as an electrostatically bound complex. © 2009 American Institute of Physics. [DOI: 10.1063/1.3212598]

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I. INTRODUCTION

In a recent publication we described a high-temperature flowing-afterglow Langmuir-probe (HT-FALP) apparatus for use in measuring electron attachment rate constants at temperatures up to 1100 K.¹ We presented data for NF_3 (300–900 K) and CH_3Cl (600–1100 K).¹ The CH_3Cl data were found to follow Arrhenius behavior in this temperature range. Extrapolation to room temperature gave a rate constant of $\sim 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. No current apparatus is capable of measuring such a low value, and even if so, the result would be surely dominated by impurities. In the present work, we have made measurements up to 1100 K for other halomethanes which also have very low attachment rate constants at room temperature: CH_2Cl_2 , CF_3Cl , and CF_2Cl_2 . Two of these cases, as with CH_3Cl , are exothermic toward electron attachment,



The remaining case, of electron attachment to CF_3Cl , is endothermic



The energies given in Eqs. (1)–(4) are those calculated using the G3 compound method² at 0 K, carried out using the GAUSSIAN-03W program.³ The G3 prescription, which includes empirical corrections based on accurate experimental energies, approximates a quantum configuration interaction calculation with a large basis set. Neutral and anion geometries are optimized at the MP2/6-31G(d) level of theory, and zero-point energies are calculated from scaled Hartree-Fock harmonic frequencies.² The G3 method is good, on average, within $\pm 91 \text{ meV}$ for enthalpies of formation of non-hydrogen-containing molecules and $\pm 49 \text{ meV}$ for hydrogen-containing molecules.⁴ Thus, on the basis of G3 calculations, Eq. (2) cannot be said to be definitely exothermic. However, the quoted exothermicities agree quite well with those derived from tabulated bond dissociation energies (DBEs) and the electron affinity (EA) of Cl, as will be seen later.

G3 calculations (Table I) show that the parent anions exist, and, in fact, CF_3Cl^- and CF_2Cl_2^- have been observed in electron attachment experiments to CF_3Cl and CF_2Cl_2 clusters.^{5,6} The parent anions are not observed for electron attachment to the monomers, in beam or thermal experiments, implying that transient parent anions are too short lived even where the gas pressure is high enough that collisional stabilization might occur. Table I includes a comparison of computational and experimental adiabatic EAs where available.^{7–9}

II. EXPERIMENTAL

The HT-FALP apparatus^{1,10} has been described previously. The HT-FALP utilizes an electron- He^+ , Ar^+ plasma

^{a)}Also at Institute for Scientific Research, Boston College, Chestnut Hill, MA. Electronic mail: thomas.miller@hanscom.af.mil.

^{b)}Present address: Department of Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

TABLE I. Calculated G3 total energies, adiabatic EAs, and C-Cl BDEs at 0 K for CH₂Cl₂, CF₂Cl₂, CH₃Cl, CF₃Cl, and dissociation fragments relevant to the energetics of attachment reactions. CHF₃ is included as relevant to comments in the text on endothermic electron attachment to CHF₃.

Molecule	Total energy (hartree)		EA neutral (eV)	BDE (eV)	
	Neutral	Anion		Neutral ^a	Anion
Parents					
CH ₂ Cl ₂	-959.371 21 ^b	-959.394 40	0.631	3.372	0.394
CF ₂ Cl ₂	-1157.787 91	-1157.808 56	0.562	3.542	0.495
CH ₃ Cl	-499.913 02 ^b	-499.917 68	0.127	3.504	0.023 ^c
CF ₃ Cl	-797.546 21	-797.558 14	0.325	3.752	0.467
CHF ₃	-338.086 56 ^b	-337.993 00	-2.546	4.577 ^d	Not stable ^e
Fragments					
CH ₂ Cl	-499.256 32	-499.281 86	0.695		
CF ₂ Cl	-697.666 78	-697.741 26	2.027		
CH ₃	-39.793 30 ^b	-39.791 85 ^b	-0.039 ^f		
CHF ₂	-238.201 32	-338.228 24	0.733		
CF ₃	-337.417 37	-337.482 98	1.785 ^g		
Cl	-459.990 96 ^b	-460.123 60 ^b	3.609 ^b		

^aThe corresponding experimental values for the neutral molecule C-Cl BDE from Ref. 28 are: 3.50 ± 0.03, 3.46 ± 0.11, 3.63 ± 0.02, and 3.79 ± 0.04 eV, respectively.

^bReferences 2 and 4.

^cThe calculated C-Cl bond length in CH₃Cl⁻ (3.776 Å), the charge distribution, and the weak BDE implies that the CH₃-Cl bond in the anion is electrostatic. While the adiabatic EA is low, the vertical EA must be close to EA(Cl).

^dBDE(CF₃-H) is listed. BDE(CHF₂-F) is calculated to be 5.471 eV.

^eExothermic toward F⁻ loss by 0.476 eV.

^fExperiment: 0.08 ± 0.03 eV (Ref. 7).

^gExperiment: 1.82 ± 0.05 eV (Ref. 8).

^hExperiment: 3.612 724 ± 0.000 027 eV (Ref. 9).

moving at high speed in a flow tube reactor entrained in a He buffer gas which contains a few percent Ar. The gas pressure ranged from 1 to 2 Torr. The plasma density decays along the flow tube due to ambipolar diffusion. At a point halfway down the flow tube, an electron-attaching gas is introduced through a four-needle injector. Following this point, the electron density decays because of electron attachment to the reactant gas and diffusion. The decay is monitored along the flow tube axis with a movable Langmuir probe. The ion products of the attachment reaction are sampled at the terminus of the flow tube and mass analyzed. The neutral products are not detected but are usually apparent from the reaction energetics. The plasma velocity is measured in order to provide the time scale for the reaction. Complete data runs for each halomethane were carried out over the available temperature range sequentially, starting with the slowest-attaching gas, to minimize contamination of the feedlines.

The electron attachment frequency ν_a is obtained from the equation describing the coupled effects of diffusion and attachment on the electron density, $n_e(t)$, as a function of time t down the flow tube axis,^{1,11}

$$n_e(t) = n_e(0)[\nu_a \exp(-\nu_a t) - \nu_D \exp(-\nu_D t)]/(\nu_a - \nu_D). \quad (5)$$

In Eq. (5), $n_e(0)$ is the electron density at $t=0$ (at the reactant inlet port), ν_D is the diffusion frequency (the ambipolar diffusion coefficient times the square of the characteristic diffusion length for the apparatus), and ν_a is the attachment

frequency. The attachment rate constant k_a is obtained by $k_a = \nu_a/n_r$, where n_r is the reactant concentration in the flow tube. In practice, Eq. (5) is used during data acquisition, and a numerical model that includes possible correction for electron-ion recombination is later fit to the data. A discussion of the rate equations including electron-ion recombination has been given earlier.¹ A recombination correction is only significant when a large concentration of molecular cations is formed from He⁺ and Ar⁺ reacting with the attaching gas since molecular cations possess large recombination rate constants, typically $\sim 3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, in contrast to the negligible ones for atomic cations. Few molecular cations are usually present in the attachment experiments. Correction becomes noticeable only when k_a is very small ($< 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) because large n_r is required to achieve a decade of decay of $n_e(t)$ in the reaction zone. The use of low $n_e(0)$ mitigates the problem. In the present work, corrections for electron-ion recombination contribution to $n_e(t)$ decay were as high as 15% at the lowest temperatures for the CF₃Cl and CH₃Cl data, but were only 2% at 900 K because the attachment rate constants were larger and the estimated ion molecule and recombination rates were lower.¹ We will assign a larger uncertainty to results for which appreciable recombination correction was required. The numerical model also accounts for ion-ion mutual neutralization, though an indiscernible effect for the $n_e(0)$ used in the present work. Rate constants for Ar⁺+CH₂Cl₂, CF₂Cl₂, CH₃Cl, and CF₃Cl were measured at 300 K by Smith *et al.*¹¹ and assumed in the

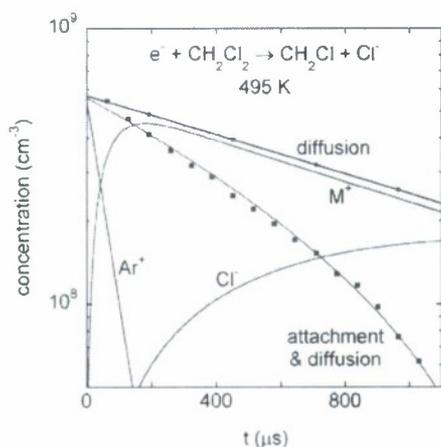


FIG. 1. Data obtained with the HT-FALP apparatus for CH_2Cl_2 ($9.5 \times 10^{12} \text{ cm}^{-3}$) at 495 K in a He/Ar huffer gas ($3.1 \times 10^{16} \text{ cm}^{-3}$) vs reaction time t . The diffusion data ($v_D=818 \text{ s}^{-1}$) were obtained in the absence of the CH_2Cl_2 . The solid curves are solutions of rate equations using $k_a=6.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. M^+ represents molecular cations produced in reaction with Ar^+ (and some He^+). The $\text{Ar}^+ + \text{CH}_2\text{Cl}_2$ reaction rate was taken to be $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and the electron recombination rate constant was estimated at $2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 495 K.

present work to decrease with temperature according to the trajectory calculations of Su and Chesnavich.¹² The electron recombination rate constant was estimated at $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} (300/T)^{1/2}$ in all cases.¹³

Figure 1 gives an example of data obtained with the HT-FALP apparatus for CH_2Cl_2 at 495 K, where k_a is small enough that a large concentration of CH_2Cl_2 is needed. Note the rapid increase in production of molecular cations (M^+ in Fig. 1) due to the reaction between Ar^+ and CH_2Cl_2 . The electron-ion correction in that case was held to an acceptable value, 14%, through the use of a low value of $n_e(0)=5.7 \times 10^8 \text{ cm}^{-3}$. The disadvantage of low $n_e(0)$ is that long reaction times correspond to low electron concentrations, which are more difficult to measure accurately with the Langmuir probe.

The estimated uncertainty in the data is $\pm 25\%$ except

for cases where significant correction is required for electron-ion recombination. If $k_a < 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, then the estimated uncertainty is $\pm 35\%$.

III. RESULTS AND DISCUSSION

Table II lists the present attachment data for CH_2Cl_2 , CF_2Cl_2 , and CF_3Cl . Figure 2 shows these data plotted in Arrhenius form in comparison with literature data from Birmingham University,¹¹ Oak Ridge National Laboratory (ORNL),^{14,15} and Boston College.¹⁶ Outside the temperature scale of Fig. 2 are data for CF_2Cl_2 obtained at temperatures of 75–170 K at the University of Rennes using a low temperature nozzle jet, which show the breakdown of Arrhenius behavior at low temperatures.¹⁷ The Birmingham University FALP data¹¹ for CF_2Cl_2 (295–590 K) lie above those of Boston College¹⁶ (293–777 K) and the present data (291–1105 K), but the Arrhenius activation energies are in rough agreement (150, 127, and 124 meV, respectively). A complete review and critical examination of data for attachment to CF_2Cl_2 , including beam experiments, has been given by Skalny *et al.*¹⁸ and Christophorou and Olthoff.¹⁹

Figure 2 and Table II include results for CH_2Cl_2 that we deduced from drift tube data of the ORNL group.¹⁴ The deduced thermal k_a merge well with the present results at higher temperature, and the Arrhenius slopes agree well (378 meV, ORNL data, and 390 meV, present data) for CH_2Cl_2 . The Boston College data show a lower Arrhenius slope of 248 meV.¹⁶ The CF_3Cl data in Fig. 2 likewise give a lower slope for Boston College data¹⁶ (316 meV) than found in the present work (406 meV).

Figure 3 shows temperature dependences for the fluorine- and chlorine-containing halomethanes along with our earlier CH_3Cl data¹ and some data from other sources.^{11,14,20} It was not possible to fit all literature data clearly on this one figure. Shown are the present data for CH_2Cl_2 , CF_2Cl_2 , and CF_3Cl , our recently published data for CH_3Cl ,¹ ORNL data for CH_2Cl_2 ,¹⁴ temperature-dependent data for CCl_4 , CFCl_3 , and CHCl_3 from Birmingham

TABLE II. Electron attachment rate constants k_a for CH_2Cl_2 , CF_2Cl_2 , and CF_3Cl obtained at temperatures T . Data for CH_3Cl were given in Ref. 1. The present experimental uncertainty is $\pm 25\%$ except for cases where significant correction for electron-ion recombination was made: If $k_a < 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, then the estimated uncertainty is $\pm 35\%$.

T (K)	$\text{CH}_2\text{Cl}_2^a k_a$ ($\text{cm}^3 \text{ s}^{-1}$)	T (K)	$\text{CF}_2\text{Cl}_2 k_a$ ($\text{cm}^3 \text{ s}^{-1}$)	T (K)	$\text{CF}_3\text{Cl}^b k_a$ ($\text{cm}^3 \text{ s}^{-1}$)
300 ^c	2.6×10^{-13}	291	1.6×10^{-9}	524	3.1×10^{-11}
400 ^c	7.0×10^{-12}	352	3.4×10^{-9}	654	2.6×10^{-10}
500 ^c	9.5×10^{-11}	400	6.0×10^{-9}	800	8.2×10^{-10}
495	7.0×10^{-11}	500	1.1×10^{-8}	898	1.3×10^{-9}
591	3.1×10^{-10}	525	1.4×10^{-8}	1004	2.5×10^{-9}
684	8.2×10^{-10}	652	2.0×10^{-8}		
790	2.0×10^{-9}	801	3.5×10^{-8}		
892	4.6×10^{-9}	900	4.5×10^{-8}		
973	5.5×10^{-9}	1004	6.3×10^{-8}		
		1105	6.1×10^{-8}		

^aThe present data extrapolated to 300 K imply $k_a=1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

^bThe present data extrapolated to 300 K imply $k_a=4.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

^cORNL data (Ref. 14) extrapolated to thermal energies.

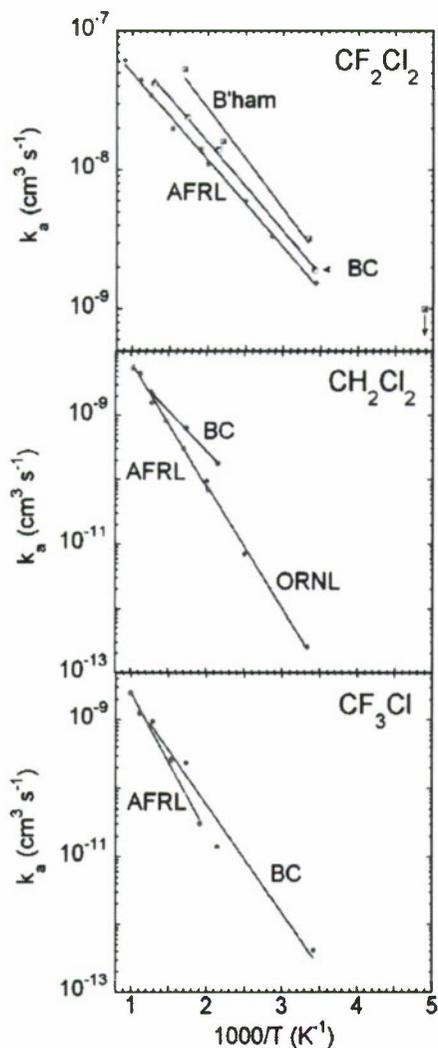


FIG. 2. Comparison of the present data (AFRL) with those of Boston College (BC, Ref. 16), Birmingham University (B'ham, Ref. 11), and Oak Ridge National Laboratory (ORNL, Ref. 14, extrapolated to thermal energy in the present work). Off scale are Rennes data (Ref. 16) at temperatures of <170 K.

University,¹¹ and a number of 300 K measurements from ORNL.²⁰ In an earlier work, we gave comparisons for attachment to CH_3Cl , for which we found an Arrhenius slope of 670 ± 70 meV.¹ The only other data at high temperatures for CH_3Cl are unpublished data from Boston College²¹ (932 and 1022 K), which agree quite well with the AFRL data. Fabrikant²² carried out *R*-matrix calculations of dissociative attachment cross sections for CH_3Cl for temperatures of 200–800 K, with absolute magnitudes pinned to experimental vibrational excitation cross sections. Rate constants were given in a later work.²³ We had to multiply the calculated rate constants by a factor of 8 to have them merge with our measurements of k_a , but the Arrhenius slopes were in acceptable agreement [611 meV (calculated) and 670 meV (experiment)].

There are four main points to be made from Fig. 3.

- (a) The halomethane data in Fig. 3 cover seven orders of magnitude in attachment rate constant.

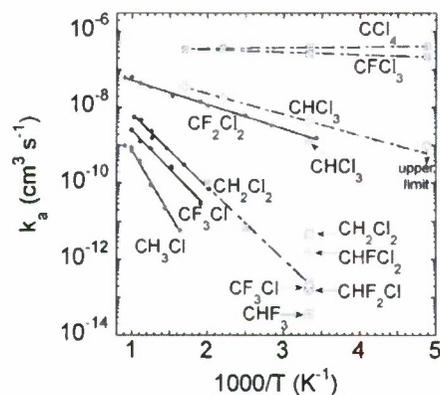


FIG. 3. Temperature dependence of halomethane electron attachment rate constants. Solid circles are the present (AFRL) data. The other data showing temperature dependences are those of Birmingham University (Ref. 11), except for CH_2Cl_2 (at 300, 400, and 500 K) which are from ORNL (Ref. 14). The points shown only at 300 K are all ORNL data (Ref. 20). The CHF_3 datum is likely in error (see text).

- (b) The temperature dependences all seem to be pointing toward a collisional rate constant (at infinite temperature) in the neighborhood of 4×10^{-7} $\text{cm}^3 \text{s}^{-1}$. Even if the extrapolations were accurate, the collisional rate constant will not be the same for all of these molecules because of their differing polarizabilities and dipole moments.
- (c) The ORNL 300 K data and the general Arrhenius picture formed from temperature-dependent data in Fig. 3 allow one to make an educated guess as to the temperature dependence for attachment to these other compounds. Generally speaking, the lower the rate constant lies at 300 K, the greater will be the temperature dependence, as if pointing toward a collisional rate constant at infinite temperature. However, we assume that the ORNL result²⁴ and the one of Fessenden and Bansal²⁵ for the slowest-attaching halomethane shown, CHF_3 , is in error because dissociative electron attachment is 2 eV endothermic, and there is no evidence for a stable parent anion. CHF_3 has a negative EA, -2.55 eV (G3 calculation, Table 1), consistent with the fact that no parent anion has been observed. Wang *et al.*²⁶ found a k_a value of 1.3×10^{-13} $\text{cm}^3 \text{s}^{-1}$ but noted that the reaction was probably endothermic and concluded that attachment to CHF_3 “is very weak or absent” at thermal energy. Jarvis *et al.*²⁷ reported no measurable electron attachment to CHF_3 within the sensitivity of their instrument (about 2×10^{-13} $\text{cm}^3 \text{s}^{-1}$). The CHF_3 data reinforce a point made earlier that extremely small k_a is difficult to measure because the slightest impurity may dominate. With three of the halomethanes we have studied, CH_2Cl_2 , CH_3Cl , and CF_3Cl , we did not measure the rate constants below 500 or 600 K because of the difficulty of measuring small k_a .
- (d) Replacing Cl atoms by either H or F atom reduces k_a , but replacement with an F atom is much less dramatic. Starting with CCl_4 , replacement with a single F barely changes k_a , but replacement with a single H changes k_a by two orders of magnitude. A second Cl replacement

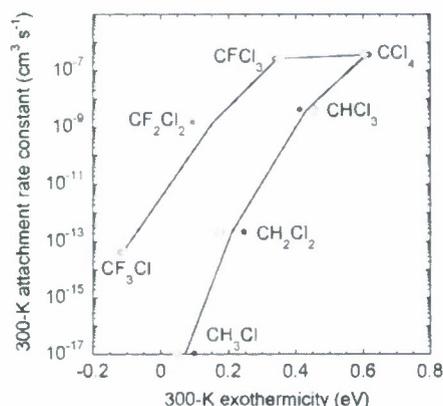


FIG. 4. Correlation of 300 K electron attachment rate constants (yielding Cl^- ion product) with reaction exothermicity (a negative value implying endothermicity). The lines are drawn to guide the eyes for molecules containing no F atoms (right) and molecules with no H atoms (left). The closed circles are data plotted vs energetics from G3 calculations (Table I). The open points are the same data plotted vs energetics deduced from BDEs minus $\text{EA}(\text{Cl})$.

with an F atom changes k_a by a larger amount and makes the reaction nearly thermoneutral. Replacement of Cl with a second H atom has a much greater effect in reducing k_a . The importance of the Cl atoms has, of course, been noted before (see Refs. 20 and 27).

These statements are illustrated in Fig. 4. The reaction energies at 298 K used in Fig. 4 were obtained (a) from G3 calculations and (b) from 298 K BDEs listed in the *Handbook of Chemistry and Physics*,²⁸ subtracted from the EA of Cl (unchanged between 0 and 298 K).⁹ The two methods agree well except for a 0.12 eV discrepancy for the CF_2Cl_2 case. However, the BDE in that case is tabulated as uncertain to ± 0.09 eV, and the G3 calculations have a similar uncertainty.

The Arrhenius plots of the present data may be used to predict 300 K values of k_a for these compounds: CH_2Cl_2 ($1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), CH_3Cl ($1.1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$), and CF_3Cl ($4.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$). The extrapolated value for CH_2Cl_2 may be compared to the 300 K estimate of $2.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ from our analysis of ORNL drift tube data.¹⁴ Considering uncertainties in both sets of data and extrapolations, the agreement is reasonable if not surprisingly so. However, three older measurements for CH_2Cl_2 are tabulated by Christophorou *et al.*²⁰ which tend to cluster around a value 20 times larger, at $4.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. For CH_3Cl , only upper limits are tabulated by Christophorou *et al.*²⁰ at 300 K, and all are consistent with the present work. For CF_3Cl , Christophorou *et al.*²⁰ tabulated four older measurements, all lying higher than the present estimate of k_a at 300 K, but not unreasonably so (5.2×10^{-14} , 7×10^{-14} , and $20 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$). In the case of CF_2Cl_2 , we were able to make a measurement at room temperature, obtaining $k_a = 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Christophorou and Olthoff¹⁹ tabulated measured values of k_a for CF_2Cl_2 with a mean value of $1.57 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 293–300 K. The Birmingham group measured $3.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for CF_2Cl_2 at 300 K.¹¹ Their results for 205–590 K are shown in Fig. 3.

The negative of the slopes²⁹ of the Arrhenius plots (multiplied by Boltzmann's constant) are used as the activation energy needed to overcome endothermicity or to surmount a barrier if the reaction is exothermic. Fabrikant and Hotop³⁰ gave an analysis of Arrhenius plots for dissociative electron attachment. For our sole endothermic case, that of CF_3Cl , their analysis indicates that the Arrhenius activation energy should be close to the threshold energy. The Arrhenius plot shown in Fig. 2 yields an activation energy of 406 ± 50 meV. The calculated endothermicity of the reaction is only 143 meV at 298 K (118 meV at 298 K), so there is apparently a barrier to attachment beyond simply the endothermicity. The barrier is likely related to the crossing point of the anion potential surface, requiring vibrational energy input to CF_3Cl in order to access the anion surface efficiently.³⁰

Relevant to the exothermic CH_2Cl_2 , CH_3Cl , and CF_2Cl_2 reactions, the Fabrikant–Hotop analysis says that the Arrhenius activation energy is lower than the barrier height, but comes closer to the barrier height if the vibrational frequency of the molecule most active in dissociation is a low frequency.³⁰ The Arrhenius activation energies are 390 ± 50 meV (CH_2Cl_2), 670 ± 70 meV (CH_3Cl), and 126 ± 20 meV (CF_2Cl_2). The C–Cl stretching frequencies are in the neighborhood of 700 cm^{-1} (87 meV), a value which is not “small” in the Fabrikant–Hotop analysis.³⁰ Thus, the anion potential surface for the three exothermic cases studied here would seem to be crossing the neutral surface at a point well above the energies given by the Arrhenius slopes. Calculation of the neutral and anion potential curves along a C–Cl bond for these molecules would be useful in understanding the measured activation energies.

We note that many other measurements have been made of the activation energy in the CF_2Cl_2 attachment reaction. In electron beam experiments, the activation energy has been obtained from the growth with temperature of the zero-energy resonance. Hahndorf and Illenberger³¹ studied the temperature dependence of attachment to several halomethanes, including CF_3Cl (no observable zero-energy resonance) and CF_2Cl_2 , between 350 and 700 K. Skalny *et al.*¹⁸ analyzed many different results for CF_2Cl_2 obtained in beam, electron swarm, and true thermal experiments to reconcile the results from the very different experiments. They compiled k_a values ranging from 75 to 777 K. The lowest-temperature data (75–171 K) are from the Rennes group,¹⁷ and the highest-temperature data included (293–777 K) are from the Boston College group.¹⁶ The Arrhenius plot containing all of these data shows Arrhenius behavior for temperatures greater than 150 K. Values of k_a below this temperature (from Rennes)¹⁷ show much less variation with temperature, which may be a result of population of only the lowest vibrational levels. Skalny *et al.* pointed out that while there is considerable difference in the activation energies determined from all of the experiments (73–195 meV), it is clear that activation energies from electron beam experiments (~ 85 meV) are lower than those from swarm and thermal experiments (~ 150 meV).¹⁸

Dashevskaya *et al.*³² gave a formula for the collisional electron attachment rate constant which serves to evaluate

the efficiency of the measured reactions. Using tabulated polarizabilities³³ and dipole moments,³⁴ the formula of Dashaevskaya *et al.* gives $k_a=3.81$ (CH_2Cl_2), 3.02 (CF_2Cl_2), 4.06 (CH_3Cl), and 2.78 (CF_3Cl) at 300 K, in units of $10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Attachment to all of these molecules is inefficient at 300 K, with CH_3Cl attaching electrons in only one of every 3.7×10^{10} collisions at 300 K.

IV. CONCLUSIONS

We have measured electron attachment rate constants for CH_2Cl_2 (495–973 K), CF_2Cl_2 (291–1105 K), CH_3Cl (700–1100 K), and CF_3Cl (524–1004 K) using a HT-FALP apparatus. The results display Arrhenius behavior in the studied temperature ranges and allow estimates of extremely small rate constants at 300 K to be made. The activation energies range from 124 meV (CF_2Cl_2) to 670 meV (CH_3Cl). The CH_2Cl_2 results merge well with rate constants measured at lower temperatures by the ORNL group, extrapolated to thermal energies.¹⁴ Arrhenius plots of the present data, taken together with attachment rate constants measured at 300 K by others (which cover seven orders of magnitude), allow one to estimate the high-temperature behavior for several other halomethanes. The attachment rate constants show a strong dependence on reaction exothermicity. G3 calculations were carried out, showing that the parent anions of CH_2Cl_2 , CF_2Cl_2 , CH_3Cl , and CF_3Cl are stable, though CH_3Cl^- exists only as an electrostatically bound complex. However, the parent anions are not observed in attachment experiments to the monomer neutrals. G3 calculations imply that CHF_3 should not undergo an electron attachment reaction at all, whether dissociatively or nondissociatively. Literature studies for CHF_3 underscore a point that extremely small attachment rate constants are difficult to measure because of interference from even trace impurities.

Note added in proof: Recent experiments with high electron energy resolution have been carried out by K. Graupner, S. A. Haughey, T. A. Field, C. A. Mayhew, T. H. Hoffmann, O. May, J. Fedor, M. Allan, I. I. Fabrikant, E. Illenberger, M. Braun, M.-W. Ruf, and H. Hotop (to be published) which show cusp structures in the electron attachment cross section for CF_2Cl_2 at thresholds for vibrational excitation of the $\nu_3(a_1)$ mode due to interaction between attachment and vibrational excitation channels, among other results.

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